

## Separation of SF<sub>6</sub>/N<sub>2</sub> Mixtures

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### Abstract

Experimental results for a combination of a separation plant consisting of modular membrane stages with a subsequent molecular sieve stage are presented. A hollow fibre membrane type and different artificial zeolites were tested. Parameters like flow, inlet pressure and pressure differentials over the membranes during separation were verified. All results concerning concentration of the mixtures were monitored online with a gas chromatograph. The maximum separation capacity of the laboratory pilot plant was 1 m<sup>3</sup>/h SF<sub>6</sub>/N<sub>2</sub> mixture. Starting from 20 vol.% SF<sub>6</sub> the remaining SF<sub>6</sub> concentration in N<sub>2</sub> outlet was below 10 ppmv.

### Abrégé

Les résultats des essais réalisés sur une installation de séparation combinée, comprenant des phases de membranes modulaires suivies d'une phase ultérieure de tamis moléculaire, sont présentés. Une membrane à fibres creuses et des zéolithes artificielles diverses ont été utilisées. Des paramètres comme le débit, la pression d'entrée et la pression différentielle sur les membranes pendant le processus de séparation ont été examinés. Tous les résultats concernant la concentration des mélanges ont été analysés en ligne avec un chromatographe en phase gazeuse. La capacité maximale de séparation de l'installation pilote de laboratoire était de 1 m<sup>3</sup>/h de mélange SF<sub>6</sub>/N<sub>2</sub>. Avec une concentration initiale de SF<sub>6</sub> de 20 pour-cent volumétrique, la concentration résiduelle de SF<sub>6</sub> dans N<sub>2</sub> à la sortie était de moins de 10 ppmv.

## Introduction

GILs (gas insulated transmission lines) provide an alternative technology for overhead lines in, for example, city centres. Mixtures of  $\text{SF}_6$  and  $\text{N}_2$  in varying percentage ratios are used in GILs, depending on the manufacturer involved.

Solvay is a world-wide supplier of  $\text{SF}_6$  and has developed a mixing station for on-site production of  $\text{SF}_6$  and  $\text{N}_2$  mixtures. In a second step, Solvay invested in research activities in order to find a procedure to separate varying concentrations of  $\text{SF}_6$  from  $\text{N}_2$ . The objectives here were to ensure that this procedure can be employed on-site, that the  $\text{SF}_6$  quality can be obtained in Solvay's  $\text{SF}_6$  ReUse concept and that the process time is acceptable to the GIL supplier. Only if solutions are found which fulfil these requirements it will be possible to successfully develop a closed loop handling of mixtures and an end of life concept for the implementation of  $\text{SF}_6/\text{N}_2$  mixtures.

## Separation Processes

There are several possible ways to separate  $\text{SF}_6$  from  $\text{N}_2$ , e.g. distillation, cryogenic methods, gas centrifuges, membranes, molecular sieves and others. For a meaningful comparison of the results of each separation process both outlets ( $\text{N}_2$  and  $\text{SF}_6$  stream) of the process must be considered. Starting from a mixture of 20 vol.%  $\text{SF}_6$  and 80 vol.%  $\text{N}_2$  which relates on almost 57 % by weight  $\text{SF}_6$  (due to the density of  $\text{SF}_6$  (6,18 g/l at 1 bar and 15°C) and 43 % by weight of  $\text{N}_2$  (density 1,170 g/l at 1 bar and 15°C) the separation process should achieve a high  $\text{SF}_6$  output concentration (> 95 % by weight) and a high  $\text{N}_2$  output purity (> 99% by weight).

The solution for GIL mixtures must include a mobile and highly efficient process, due to the large volumes to be handled and the necessity to separate the mixture at the point of usage. These additional circumstances play a very important role in the selection of the right separation process. Desirable parameters include low

maintenance requirements and a separation process which is not affected by environmental issues (no difference when working in cold or warm climate zones etc.). This paper describes some traditional methods (e.g. distillation, cryogenic methods) under practical aspects and more detailed "new" methods like membranes and molecular sieves.

## Pressurised Distillation

Pressurised Distillation of  $\text{SF}_6/\text{N}_2$  includes separation of  $\text{SF}_6$  by means of low temperature condensation in a liquid phase and of  $\text{N}_2$  in the gas phase. Altunin [1] describes the phase equilibrium of the system  $\text{SF}_6/\text{N}_2$ . Comparable results are obtained by calculations with a Peng-Robinson [2] cubic equation of state. When performed in a single loop at  $-80^\circ\text{C}$  and 30 bar, the process yielded an  $\text{SF}_6$  output with 97% by mass of  $\text{SF}_6$  in the liquid phase and 85 % by mass of  $\text{N}_2$  in the gas phase. This process can be optimised by using several steps to enrich the outlet concentrations. Nevertheless, this process involves high energy consumption for compressing and cooling the gas mixtures (even if heat exchangers are used and thermal energy is reused). It will be difficult to construct a mobile plant which is able to separate large quantities and achieve a  $\text{N}_2$  purity of 99 % by weight.

## Cryogenic methods

Cryogenic methods are cooling down the  $\text{SF}_6/\text{N}_2$  mixtures at ambient pressure to the melting point ( $-51^\circ\text{C}$ ) or below. These are temperatures where  $\text{SF}_6$  attains its solid state and looks like "snow". The vapour pressure above the sublimated  $\text{SF}_6$ , e.g. at  $-80^\circ\text{C}$  is 320 mbar [3]. This process can as well be optimised by working in cascades and reducing the working pressure. This means that a relatively high amount of energy is needed as well to cool down the gas mixture and liquefy the  $\text{SF}_6$  afterwards. In addition, the difficult separation process requires an advanced process engineering. Cryogenic methods are not suitable for

mobile applications, if large amounts of gas mixtures, e.g. 250 m<sup>3</sup>/h, have to be separated.

### Gas Centrifuges

Gas centrifuges are the most efficient way to separate SF<sub>6</sub> from N<sub>2</sub>. This process is used for the enrichment of uranium. This is also the reason why the gas centrifuges market is very restrictive. Apart from this issue, gas centrifuges are extremely expensive and not suitable for mobile application.

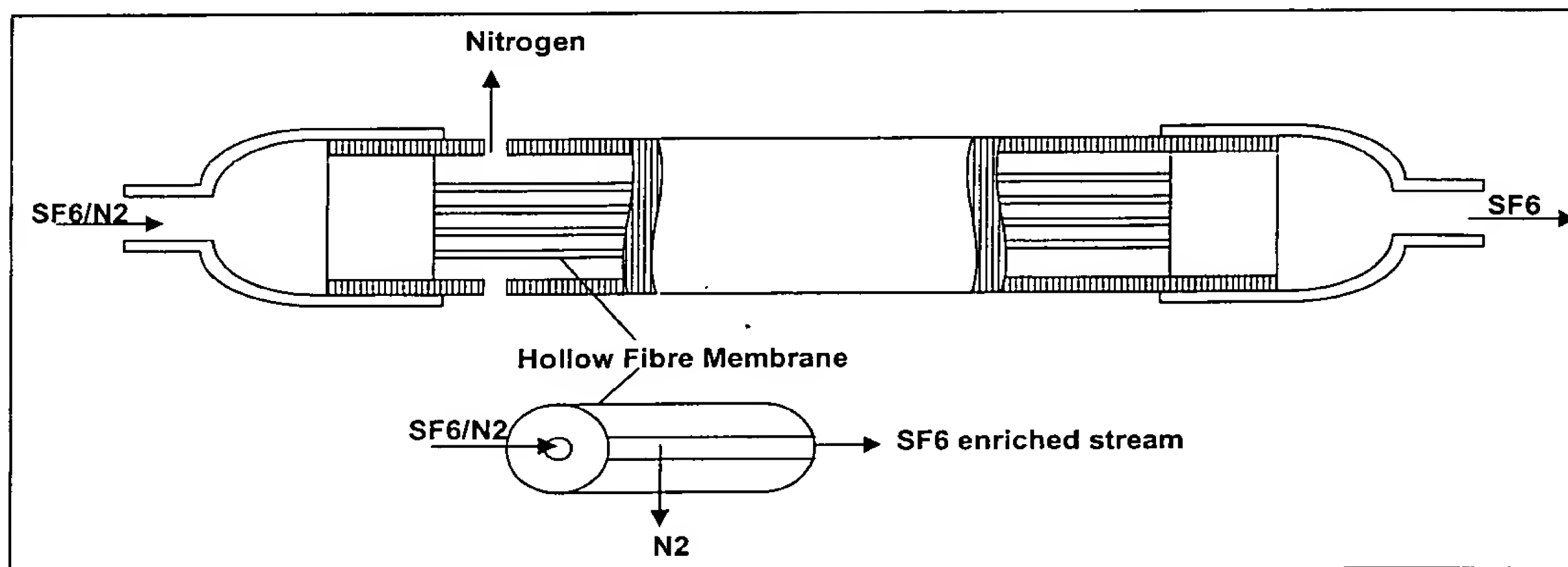
### Membrane Technology

It is a well known procedure to use different types of membranes (e.g. asymmetric, micro-porous, homogeneous and liquid membranes, electrically charged barriers etc.) for different separation processes. For gas separation mainly homogeneous membranes are used. What is important for the separation of gas mixtures is permeation through a membrane. There are gases, e.g. He, Ne, etc. which pass through a membrane very fast and others like Xe, N<sub>2</sub>, CO, and SF<sub>6</sub> which pass slowly [4] through polymer membranes.

no matter if it is pressurised on the feed side or if a vacuum on the permeate side is used. Another important criterion for the application of the membrane process apart from permeability is the selectivity of the membrane [5]. In order to obtain higher selective membranes than polymer or cellulose membranes, they are coated with carbon sieves or zeolites.[6][7][8][9]

For industrial applications of gas separation processes homogeneous membranes are preferable, as they reach a sufficient purity of the relevant product in different applications. Homogeneous membranes are already used to separate various gases, such as separation of N<sub>2</sub> from air by means of hollow fibre membranes. The hollow fibre membranes are produced in very thin pressure resistant tubes [5]. Several of these tubes are combined parallel to the axis which gives a large membrane surface while keeping the volume small. These hollow fibre membranes are able to separate SF<sub>6</sub> from N<sub>2</sub> at an efficiency that depends on the process parameters.

The separation conditions for membranes are defined by the flow, the pressure difference within the membrane and the



Picture1: Schematic of a hollow fibre membrane

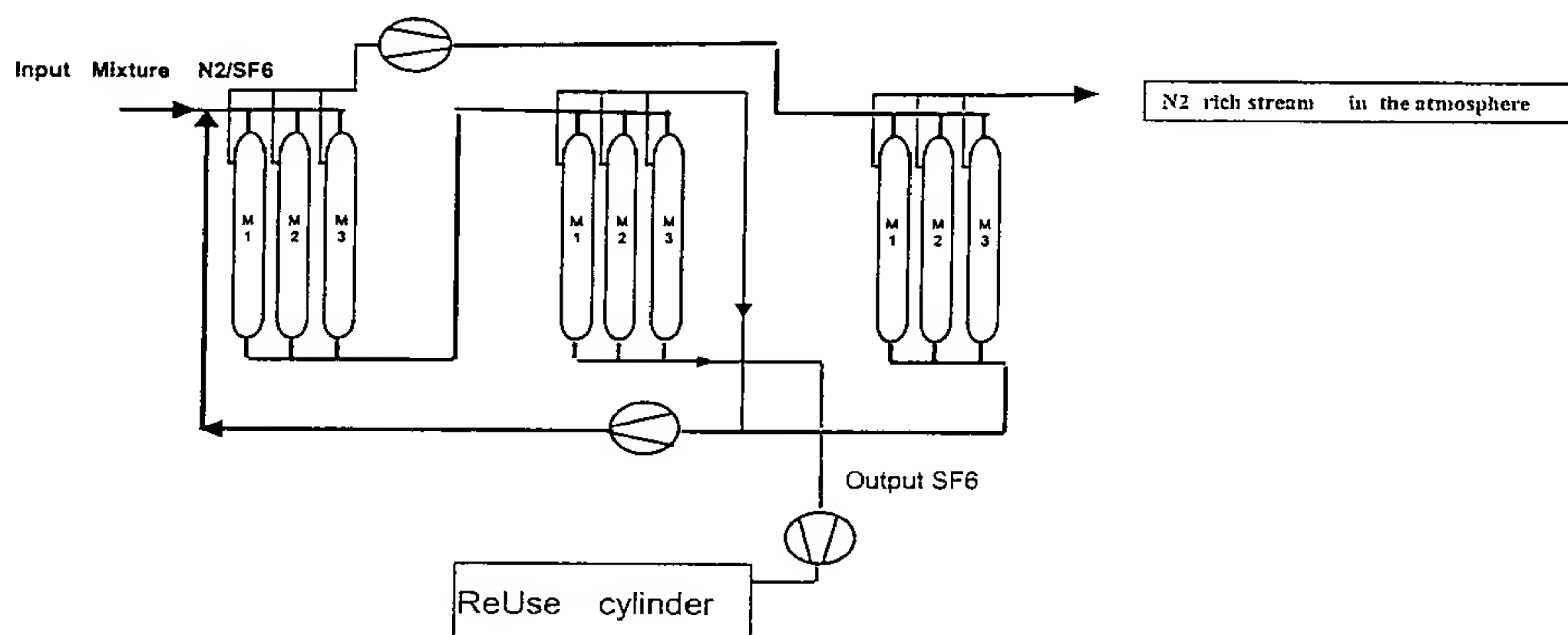
This diffusion results from the partial pressure difference on both sides of the membrane. The membrane characteristic for the separation works in the same way,

outlet pressure, temperature and treatment time. These parameters have to be optimised for each separation problem.

The  $\text{SF}_6/\text{N}_2$  mixture or feed stream is separated in a permeate stream (rich in  $\text{N}_2$  at ambient pressure) and a product stream (rich in  $\text{SF}_6$  at a higher pressure).

mixture was studied from 5 to 13 bar. At higher pressures the separation of  $\text{SF}_6$  from  $\text{N}_2$  using this hollow fibre membrane with a constant flow showed a better product

#### $\text{SF}_6/\text{N}_2$ Membrane Separation Plant



SFD-AA Mpf

Picture 2: Membrane process pilot plant

With a single membrane stage, the product stream already attains concentration levels of between 40 and 60 vol.% of  $\text{SF}_6$ . If this product stream is reintroduced in a second membrane stage a product stream of more than 80 vol. % of  $\text{SF}_6$  could be achieved. The permeate of the second stage is then introduced in the feed stream of the first stage because of a similar  $\text{SF}_6$  concentration.

With a single membrane stage a concentration in the permeate stream of only 3 vol.% of  $\text{SF}_6$  in  $\text{N}_2$  could be achieved. If this permeate is reintroduced in a second membrane stage, the  $\text{SF}_6$  concentration is lower. The non selective hollow fibre membranes can be optimised to obtain up to 0.2 vol.% of  $\text{SF}_6$  in the stream that is rich in  $\text{N}_2$  (permeate), although at the same time a less favourable  $\text{SF}_6$  concentration is achieved in the product stream.

#### Experimental design and results

All concentrations in the a.m. membrane process (picture 2) were monitored online by means of a gas chromatograph (GC). The experimental trials were performed on industrial available membrane units with a flow of  $1 \text{ m}^3/\text{h}$ . The inlet pressure of the gas

enrichment for the stream rich in  $\text{SF}_6$  and simultaneously the  $\text{SF}_6$  concentration in the permeate stream increased as well.

The pressure difference in the membrane cartridge is negligible for the separation of  $\text{SF}_6/\text{N}_2$  mixtures. The gas mixture flow in the membrane unit is an important factor for the permeate (high flow rates are better) and for the product (low flow rates are better).

The working parameters for the hollow fibre membranes can be optimised in two ways. First, if the parameters are optimised for the permeate outlet (stream rich in  $\text{N}_2$ ) this would mean high flow rates and a relatively low inlet pressure to minimise  $\text{SF}_6$  concentration. If, in contrast, the parameters are optimised for the product high flow rates and a relatively high inlet pressure are required to increase the  $\text{SF}_6$  concentration as much as possible.

The process know-how lies in the combination of membrane surfaces, membrane arrangements, flow and pressure parameters in a way to achieve the required concentrations for  $\text{N}_2$  and  $\text{SF}_6$ .

This technology yields an optimum for the  $\text{SF}_6/\text{N}_2$  separation from 10 to 90 vol.% of  $\text{SF}_6$  (inlet) down to 1 vol.% of  $\text{SF}_6$  remaining in the  $\text{N}_2$  (outlet). Further reductions of the  $\text{SF}_6$  content in  $\text{N}_2$  by means of polycarbonate hollow fibre membranes are

not recommended because the increase in the separation efficiency is relatively small compared to the costs of additional membrane cartridges. For a separation of SF<sub>6</sub>/N<sub>2</sub> mixtures with less than 1 vol.% molecular sieves are a better solution.

## Selective molecular sieves

Selective molecular sieves (adsorbers) are commonly used for gas separation in pressure swing adsorption processes, e.g. removing chlorinated organic compounds from air. There are also molecular sieves which adsorb  $\text{SF}_6$  and have already been described by Daniel Berg and William M. Hickam in 1961 (13X molecular sieve) [10]. Molecular-sieve zeolites are crystalline aluminosilicates of elements from group IA and group IIA such as sodium, potassium, magnesium, and calcium. Chemically, they are represented by the empirical formula:



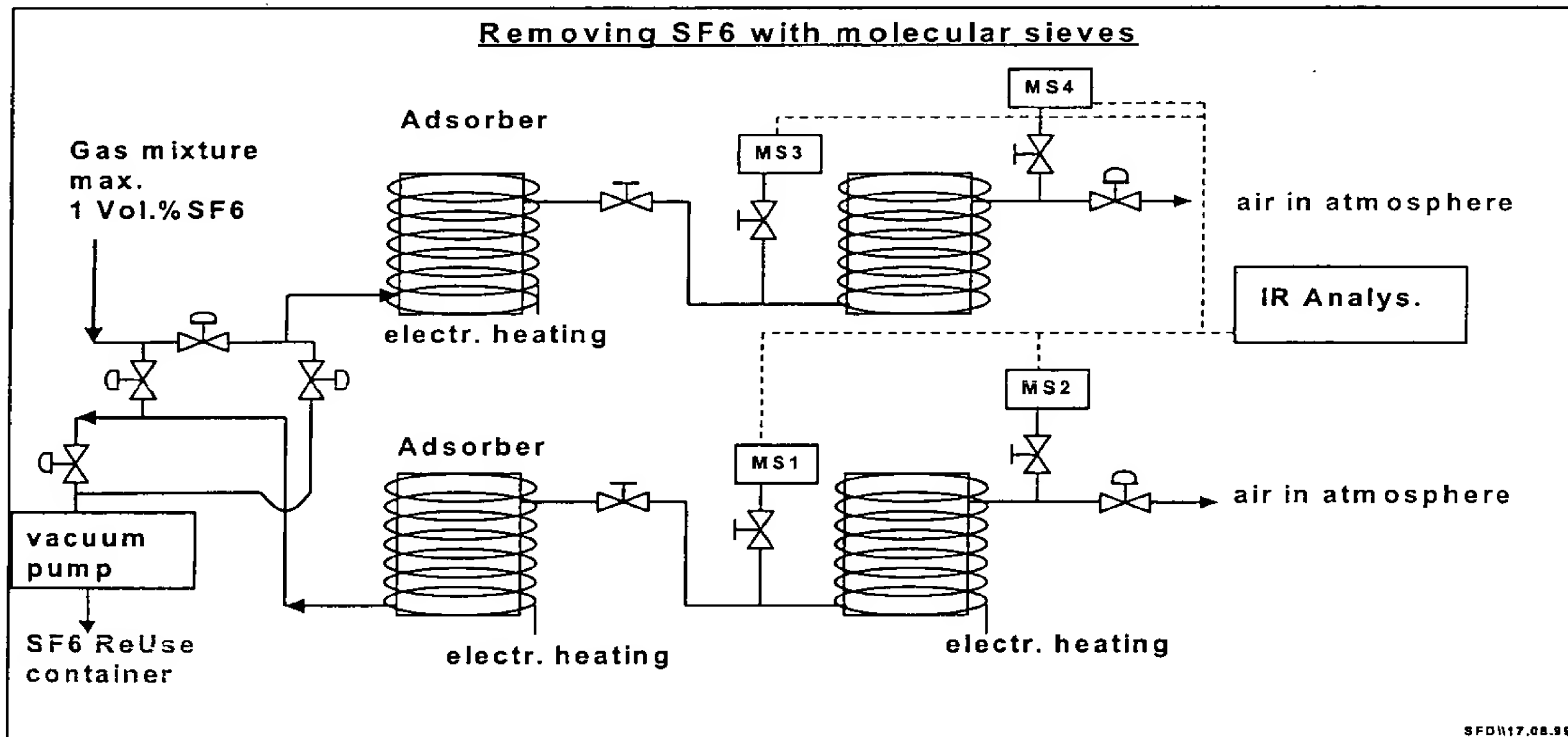
	$d_m$	$l$	$w$	$h$
SF <sub>6</sub>	0.522	0.58	0.5	0.49
N <sub>2</sub>	0.258	0.33	0.23	0.23

Table 1: Dimensions of penetrant molecules (in nm) [12]

The comparison of the dimensions shows that a molecular sieve must be used which adsorbs  $\text{SF}_6$  and lets  $\text{N}_2$  pass.

In the past, the commercially available zeolites were mainly hydrophilic due to their lower  $\text{SiO}_2$  content. Modern production processes for zeolites have made it possible to reduce the  $\text{Al}_2\text{O}_3$  content in the zeolites. These zeolites that are rich in  $\text{SiO}_2$  have hydrophobic characteristics [13]. With these zeolites  $\text{SF}_6$  can be removed from  $\text{N}_2$  down to a level of 10 ppm and the zeolites regenerated by thermal desorption.

The resulting concentration of the released SF<sub>6</sub> could easily be more than 90% by



### Picture 3: Molecular sieve process

These zeolites with a specific pore size and a specific module (ratio on  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) are able to adsorb  $\text{SF}_6$ . This becomes clear when comparing the molecule diameters of  $\text{SF}_6$  and  $\text{N}_2$ .

weight, depending on the parameters (like temperature and vacuum) and the zeolite.

The concentration of SF<sub>6</sub> delivered by the molecular sieves depends on the other gases present in the mixtures. Therefore, others gases like CO<sub>2</sub> are in competition with SF<sub>6</sub> which means that they adsorb and



release under the same process parameters.

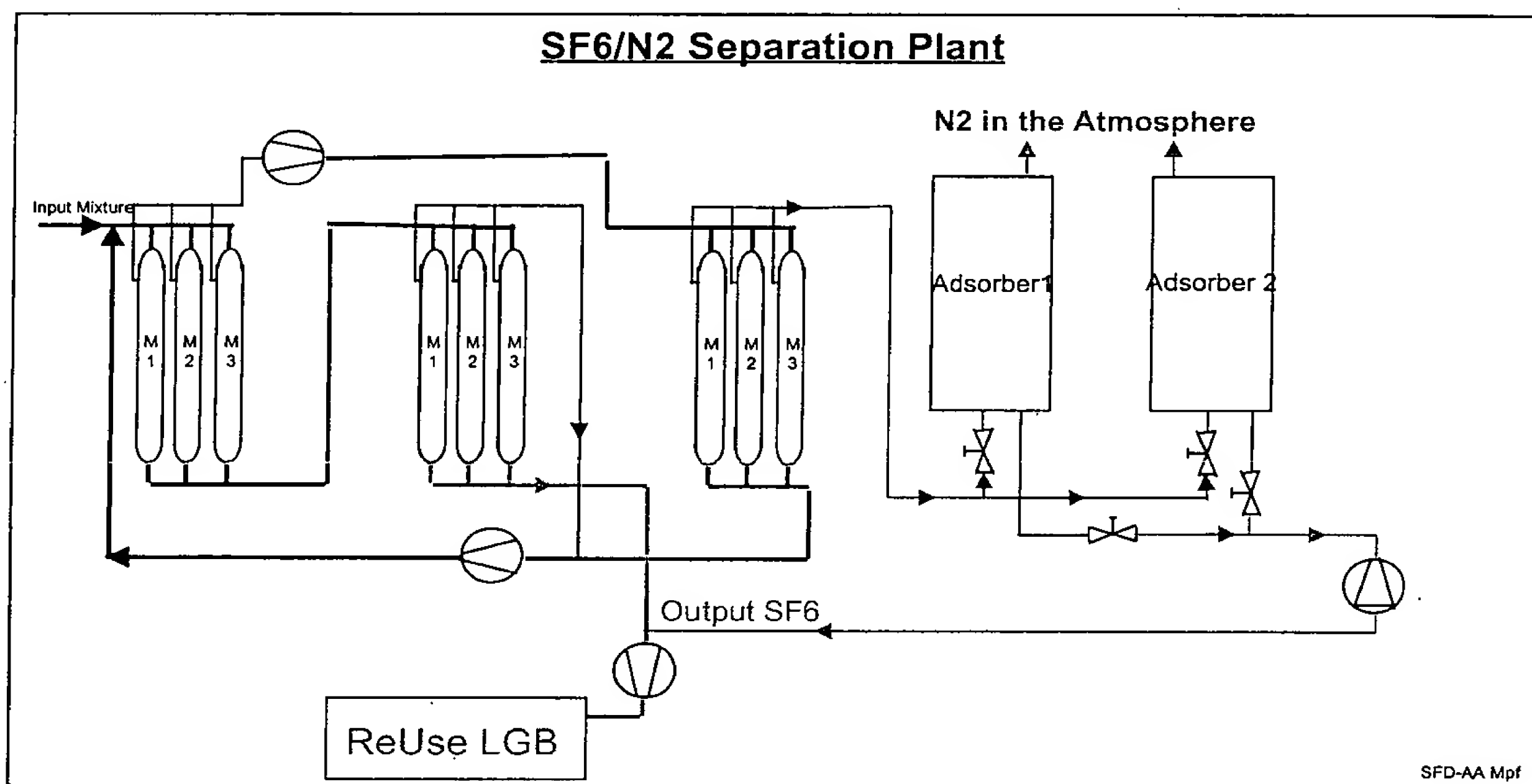
The capacity of the molecular sieve ranges from 1 to 3 % by weight. So, for 1 kg of 100 % SF<sub>6</sub> between 40 and 100 kg of molecular sieve is necessary (corresponds to a molecular sieve volume of 28 – 70 l).

Picture 3 shows a molecular sieve process with two adsorber lines in parallel. This modification allows a continuous adsorption process. While one adsorber line is working, the other one is regenerated. The whole process is controlled by means of an infra red (IR) analyser. This IR analyser on-line monitors the SF<sub>6</sub> concentration downstream of each adsorber. If, for example, the SF<sub>6</sub> value at MS4 is above 10 ppmv, the analyser sends a signal to the automatic valves to switch to the other adsorber line. The regeneration of an adsorber line is a two step process. In the first step a vacuum

130°C. During this heating process, the adsorbed SF<sub>6</sub> is desorbed and filled into a storage vessel or ReUse container by means of a vacuum pump and a compressor. If the vacuum pump reaches a certain value, e.g. 50 mbar, the desorption process is finished. The temperature of 130°C is necessary to prevent moisture from building up in the adsorber. This process is preferably used for low SF<sub>6</sub> concentrations (i.e. 2 vol.% of SF<sub>6</sub> or lower) and reasonable flow rates, if a mobile separation concept is required.

## Combination of membranes and molecular sieve

In this chapter some new results obtained with a combination of a separation plant featuring modular membrane stages and a subsequent molecular sieve stage are



Picture 4: Combination of membranes and molecular sieve

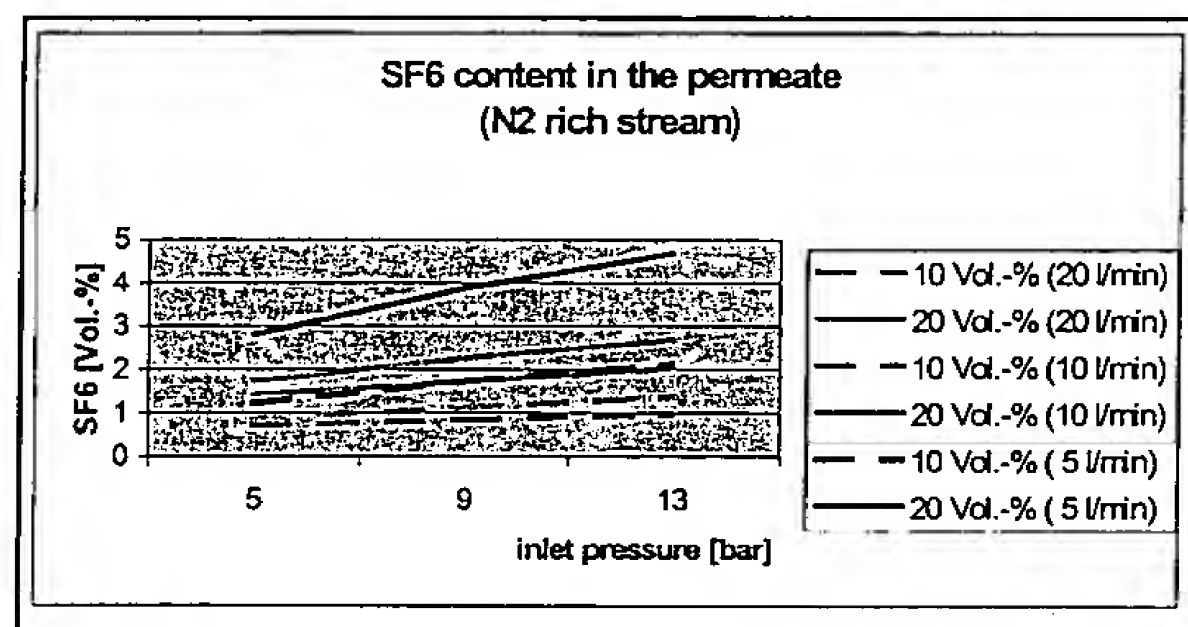
pump removes the residual gas mixture from the plant. This gas mixture will not be released, but is reintroduced into the other adsorption line. In the second step the electrical heating increases the temperature of the adsorber material to a level above

presented. A hollow fibre membrane type and different artificial zeolites were tested.

Parameters like flow, inlet pressure and pressure differentials over the membranes during separation were studied. All results concerning the concentration level of the mixture were monitored online using a gas chromatograph.

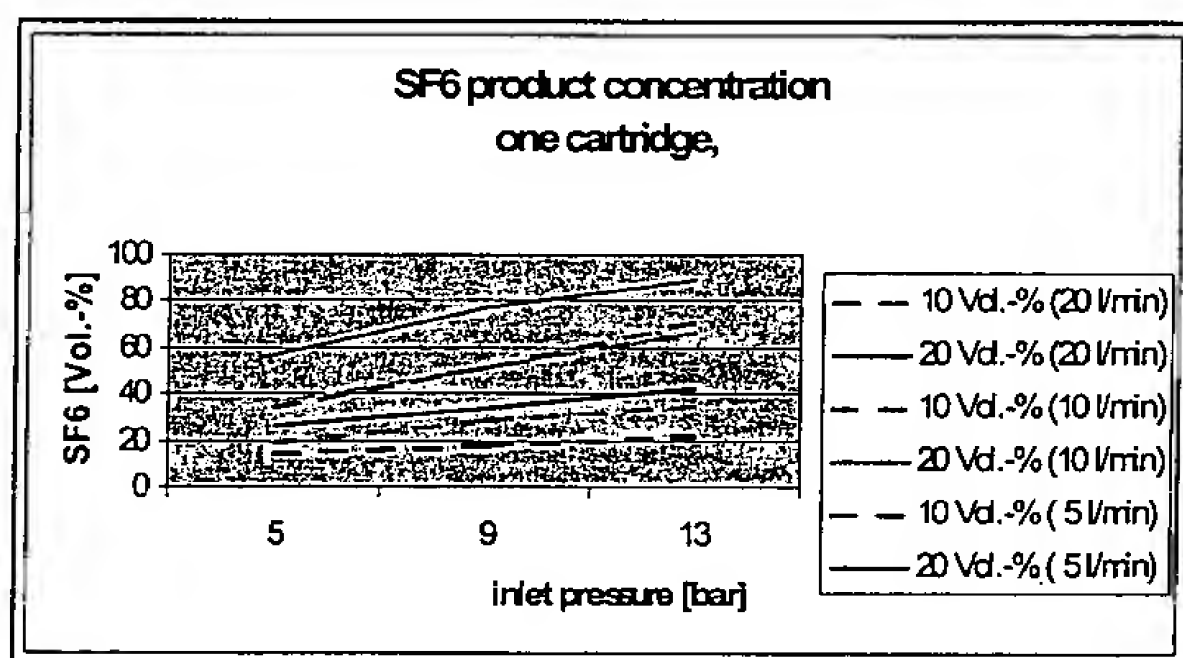
The maximum separation capacity of the laboratory pilot plant was 1 m<sup>3</sup>/h of SF<sub>6</sub>/N<sub>2</sub> mixture.

The concentration levels and separated gas streams were checked by means of a gas counter, flow meters and the corresponding sample valves for GC measurements. It was possible to balance all SF<sub>6</sub> streams.



Picture 5: Permeate results with one membrane cartridge

The outlet concentration after the last membrane stage in the permeate stream is 1 vol.% of SF<sub>6</sub> in N<sub>2</sub> when starting with an SF<sub>6</sub> concentration of 20 vol.-%



Picture 6: Product results with one membrane cartridge

The outlet concentration after the last membrane stage in the product stream (only membrane stages) could be enriched to up to 90 vol.% of SF<sub>6</sub>.

A subsequent purification of the permeate stream with molecular sieves resulted in SF<sub>6</sub> concentrations of less than 10 ppmv in N<sub>2</sub>. The combination of these two technologies is preferable because the permeate pressure and the inlet pressure for the molecular sieves are harmonised.

This two-stage solution achieves a high level of separation efficiency in each stage because each technique is used in its own optimum range of separation.

With these techniques mobile separation plants are imaginable from 1 m<sup>3</sup>/h to up to 250 m<sup>3</sup>/h with an SF<sub>6</sub> content of up to 50 vol.-%.

Before this combination of membranes and molecular sieves processes can be used possible decomposition products have to be removed, e.g. via a filter. Solvay has not yet carried out any trials on the reduction dependency on the lifetime of membranes and molecular sieves, and the content of decomposition products (such as SOF<sub>2</sub>, SO<sub>2</sub>, HF).

### Resume

This paper of course does not cover all possible technologies or combinations of technologies for the separation of gas mixtures. The approach of the paper is to give an overview of separation concepts for SF<sub>6</sub>/N<sub>2</sub> mixtures. As Solvay has already established the SF<sub>6</sub> ReUse concept it is necessary within the Responsible Care Program to assist in implementing a closed loop concept for SF<sub>6</sub>/N<sub>2</sub> mixtures in gas insulated transmission lines (GILs).

The modular arrangements of processes for membranes and molecular sieves allow tailor made solutions for each separation problem. Due to the high "reactive" separation surfaces of both processes a mobile separation plant concept is also feasible for the separation of high volumes of mixtures, e.g. 250 Nm<sup>3</sup>/h. Both processes are already available on an industrial scale and have been used for several years (but in different applications). The periphery equipment (e.g. compressor, vacuum pump etc.) is relatively simple, which allows an easy handling. The process can be realised with fully automatic equipment or with fewer electronic control devices.

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